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BULLETIN OF THE RESEARCH COUNCIL OF ISRAEL

Section C TECHNOLOGY

Bull. Res. Counc. of Israel. C. Techn.

Incorporating the Scientific Publications of the Technion — Israel Institute of Technology, Haifa

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THE EFFECT OF DEFLOCCULANTS ON THE VISCOSITY OF LOCAL CLAY SUSPENSIONS*

J. BARTA

Division of Industrial Chemistry, Technion – Israel Institute of Technology, Haifa

ABSTRACT

Ceramic suspensions were prepared from local clays, quartz and water. The clays used were Clay No. 1 and Flint Clay from Wadi Ramon, and Clays No. 50 and 53 from Wadi Hatira. The effect of seven deflocculants on the viscosity of the slips was studied.

Clays No. 1 and 53 and Flint Clay were easily deflocculated, while Clay No. 50 required preliminary washing. The most effective deflocculants were sodium hexametaphosphate, sodium pyrophosphate, and a mixture of sodium carbonate and sodium silicate (1:1).

Sodium carbonate and sodium silicate had a lesser effect, while sodium gallate and sodium humate required high concentration to obtain maximum deflocculation.

INTRODUCTION

In the last few years, significant deposits of clays have been discovered in the Negev, mainly in Wadi Hatira and Wadi Ramon[1]. A few studies of the unfired properties of these clays have been reported. Thus, Mitzmager and Lender[2] report that soluble salts, sand and possibly feldspar are removed by simple washing methods from Clays No. 50 and 53. The soluble salts of Clay No. 1 and Flint Clay can be removed by wet grinding and tumbling; the titanium and iron oxide content of the clays is not affected by washing.

Tauber and Leitner[3] studied the effect of sodium carbonate, sodium silicate, sodium humate and tanium, at a concentration of 0.8% electrolyte, on slips (ceramic suspensions) prepared from Clay No. 53, and concluded that sodium humate is the most suitable deflocculating agent. Washing of the clay improved the effect of the electrolytes.

The purpose of the present work was a general investigation of unfired properties of those of the local clays which are of importance in the manufacture of ceramic ware. The present paper deals with the effect of deflocculants on the viscosity of slips.

The clays studied were Clay No. 1 and Flint Clay from Wadi Ramon and Clays No. 50 and 53 from Wadi Hatira.

ANALYSIS OF THE CLAYS

The chemical analysis of the clays, as given by Landsberg[1], is shown in Table I. There is some variation from sample to sample, but this is irrelevant for the purpose of this study.

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* The paper is part of a thesis submitted in partial fulfilment of requirements for the degree of Master of Science in the Faculty of Chemical Technology.

Received June 7, 1957.

TABLE I

Chemical analysis of clays (per cent)

Sample	Clay No. 1	Flint Clay	Clay No. 50	Clay No. 53
SiO_2	48.2	45.4	54.9	52.1
Al_2O_3	37.5	39.7	29.8	33.4
Fe_2O_3	0.5	0.4	3.1	2.1
TiO_2	1.2	0.8	0.4	0.1
CaO	0.5	traces	0.2	0.6
MgO	0.4	0.2	traces	0.4
H_2O	12.3	13.7	11.1	11.3
Na_2O	n. d.	n. d.	1.2	n. d.
K_2O	n. d.	n. d.	0.04	n. d.
Total	100.6	100.2	100.74	100.0

According to Ben-Tor[4], Clays No. 50 and 53 consist mainly of kaolinite, quartz and some montmorillonite. X-ray diffraction analysis[4] shows that the major constituents of Flint Clay are kaolinite, boehmite and diaspore and that the minor constituents are anatase and rutile. Clay No. 1 contains kaolinite and quartz as major constituents and halloysite, diaspore, rutile, anatase and brookite as minor constituents.

Quantitative determination of quartz by the X-ray diffractometric technique was carried out, using calcium fluoride as internal standard, giving the following results:

Clay No. 1	16%
Flint Clay	No quartz
Clay No. 50	24.5%
Clay No. 53	17.0%

Soluble salts, *p*H, air-dry moisture content and cation-exchange capacity were determined by standard procedures, and the results are summarised in Table II.

TABLE II

Analysis of local clays (results are referred to oven-dry basis)

Sample	*p*H*	Water-soluble Ca + Mg meq/100 g	Sulphate %	Chlorine %	Moisture (110°C) %	Cation exchange capacity** meq/100 g clay
Flint Clay	7.35	4.96	0.16	0.03	1.04	4.8
Clay No. 1	7.00	4.26	0.09	0.53	2.49	6.1
Clay No. 50	5.10	1.5	0.08	1.47	4.15	8.9
Clay No. 53	6.75	4.06	0.10	0.40	3.48	7.7

* Clay/water ratio 1:10

** In accordance with the procedure outlined by Graham and Sullivan[5]

Mechanism of deflocculation

The mechanism of deflocculation of clay suspensions has been the subject of extensive research. A review of different theories is given by Eitel[6] and Norton[7].

There is general agreement among investigators that the clay particle in aqueous media is a colloidal negatively-charged micelle surrounded by a cloud of positive ions, forming as a whole a "diffuse double layer". This double layer may be regarded as an electrical condenser system whose potential difference is a measure of the forces of repulsion between the similarly-charged clay particles. The Gouy-Chapman theory assumes that the "total potential drop caused by the double layer occurs in the outer liquid portion, which consists of a diffuse layer of ions". Stern's theory assumes that "part of the ions remain attached to the surface, and part are free to move"[8]. In this case "the total potential drop is divided into a potential over the diffuse part of the double layer and [a potential] over the molecular condenser"[9].

The potential drop is "directly proportional to the number of ions adsorbed on the surface of a particle and to the average thickness of the cloud of countering ions surrounding the surface layer; it is inversely proportional to the dielectric constant of the suspending liquid"[10].

By adding hydroxides of alkali metals to a suspension of kaolinite in water, preferential adsorption of the hydroxyl anions on the kaolinite surface takes place (increase of the electric charge on the particle): the average thickness of the double layer is increased on account of the high equilibrium distance of the alkali cations, and a slight excess of hydroxyl ions brings about an appreciable reduction in the dielectric constant of the suspending liquid[7].

The increased potential difference results in greater repulsion forces between the particles, and these in turn reduce the force required to shear the system. This seems to account for the considerable reduction in the viscosity of the system.

It was pointed out by Kiefer[11] that the added electrolyte may reduce the amount of water bound to the clay micelle, thus increasing the "free water," i.e. the fluidity of the system. The factor which would tend to impede deflocculation is therefore the presence of polyvalent cations and anions other than hydroxyl; these have to be removed by washing, converted into non-ionised salts (with sodium carbonate or sodium silicate), sequestered (with polyphosphates) or buffered with protective colloids (humic or gallic acids)[7,10]. The effect of the polyvalent anions, such as the polyphosphates, humates, tannates, etc., can be explained by their structural configuration "yielding spatially extensive anions in which, in the ionised state, the negative charge is rather uniformly distributed." They "plate" the clay particles by preferential adsorption and yield maximum deflocculation due to the mutual repulsion of clay particles which have like charges[12]. Differences in the effect of deflocculants on different clays are explained by different mineralogical composition, particle size distribution, base exchange capacity, humic material content[13,14] and soluble salts content[7].

Experimental procedure

Samples of about 100 kg of each clay were obtained from Na'aman Works, Ltd., Haifa. The clays were crushed in a jaw-crusher to a maximum particle size of 3.0 mm. During crushing, one-fourth of the total quantity was continuously withdrawn to obtain a gross sample of about 35 kg. The gross sample was thoroughly mixed by tumbling. All slips were prepared from these gross samples; a laboratory sample of about 3 kg was obtained from the gross sample, ground to 100 mesh in a Fisher motor-driven mortar grinder, and used for analysis as shown in Table II.

The effect of deflocculants on the apparent viscosity of clay slips prepared from 25% clay, 25% quartz and 50% water was studied with the aid of a Model MV Brookfield Viscometer, 20 rpm at 25 ± 0.2°C.

The deflocculants used were as follows: sodium carbonate—C. P. Baker; sodium silicate—Atlis, Hadera, analysed as $Na_2O \times 3.4\ SiO_2$; sodium humate—prepared from Huleh peat; sodium gallate—prepared from Eastman Kodak gallic acid (technical); sodium hexametaphosphate—Ayalon and Etzioni Ltd., Haifa; sodium pyrophosphate—C. P. Baker; mixture of sodium carbonate and sodium silicate 1:1.

Clays No. 50 and 53 were blunged by means of a Lightning Model V Mixer (Mixing Equipment Co.) with a three-blade marine propeller, 2000 rpm; 95% of these clays passed through sieve No. 120, and this portion was reserved for future work. Clay No. 1 and the Flint Clay had to be ball-milled before passing a 120-mesh sieve. The quartz (obtained from Harsa Works Ltd., Haifa) was ground to pass a 120-mesh sieve, washed and dried before use. Particle size analysis of the clays and quartz as used in the experiments is given in Tables III and IV. Slips were prepared from all

TABLE III

Particle size analysis of clays as used in the experiments (hydrometer method)

Sample	Percentage below stated size (equivalent spherical radius, microns)								
	125	36	25	16	9	5	2.5	1	0.5
Flint Clay	100	88	79	67	59	49	42	35	26
Clay No. 1	100	63	58	55	50	42	40	30	23
Clay No. 50	100	93	89	84	78	69	60	51	41
Clay No. 53	100	96	93	91	87	79	68	54	40

TABLE IV

Screen analysis of quartz

U.S. standard sieve mesh	Percentage through screen
120	100
140	87.4
200	65.4
325	8.1

clays and barium carbonate was added in accordance with the SO_4^{--} content of the slip. The slip was then aged for four days. Electrolytes were added in increasing amounts from 0 to 5% (calculated on an oven-dry clay basis) and the viscosity determined.

RESULTS AND CONCLUSIONS

The effect of the deflocculants on the clay slips is shown in Figures 1 to 5.

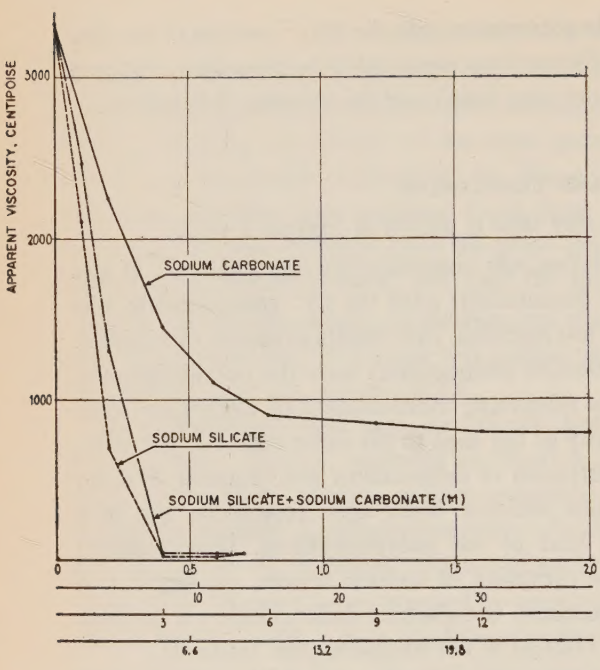
In the case of Clay No. 50, deflocculation was unsatisfactory (see Figure 3). It was then washed (by repeated mixing and decantation) until the Cl^- concentration was reduced from 1.47% to 0.35%, and the test repeated, with results as shown in Figure 4.

It can be concluded that the most effective deflocculants were the polyphosphates, permitting a minimum viscosity at the minimum concentration of electrolyte used. Organic electrolytes reduced the viscosity of the slips to the same extent as the polyphosphates, but a much higher concentration of deflocculant was required. Sodium carbonate and sodium silicate were less effective when used separately, but in a mixture of 1:1 the effect resembled that of the polyphosphates. Deflocculation curves show that in all cases, with the exception of sodium silicate, no increase in slip viscosity is caused by excess deflocculant. Satisfactory deflocculation is possible in all clays, provided the soluble salts content is not excessive (see Table II).

Comparing the effect of the deflocculants on an equivalent basis for each clay, there is generally good agreement between the quantity of deflocculant needed for maximum deflocculation, with the exception of sodium carbonate and sodium pyrophosphate (calculated as $P_2O_7^{4-}$ anion). The data reported here are in agreement with those obtained for sodium silicate and sodium carbonate by Currier[15], Norton[7] and Kiefer[11], for sodium pyrophosphate by Tchillingarian[12] and for sodium humate by Kiefer[11].

ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to Prof. H. Heimann, Dean of the Faculty of Chemical Technology, under whose supervision the work was carried out, to Prof. G. Kirkendale of Alfred University, to Mr. R. Hammer of the Ceramic Research Association of Israel, and to Mr. I. Ungar of Na'aman Works Ltd., for their helpful suggestions.



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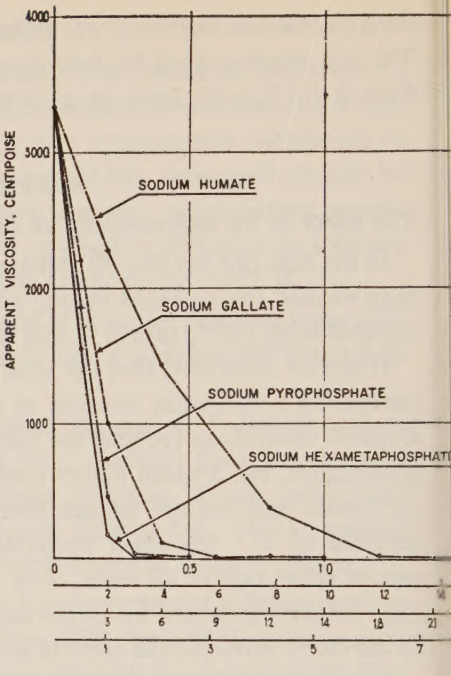

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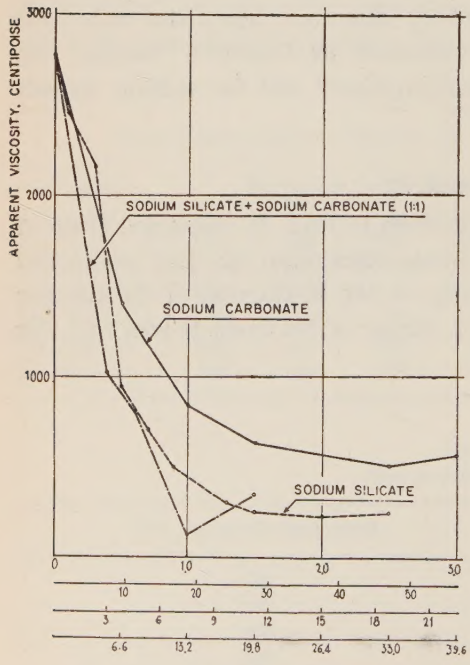
Figure 1. Effect of deflocculants on flint clay*



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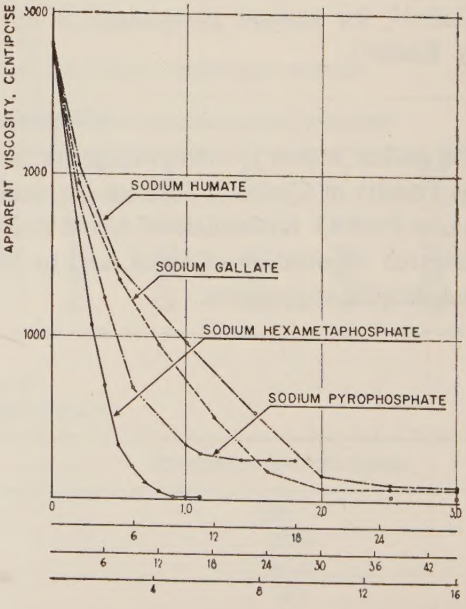

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Figure 2. Effect of deflocculants on Clay No. 1*

* See Key on p. 214

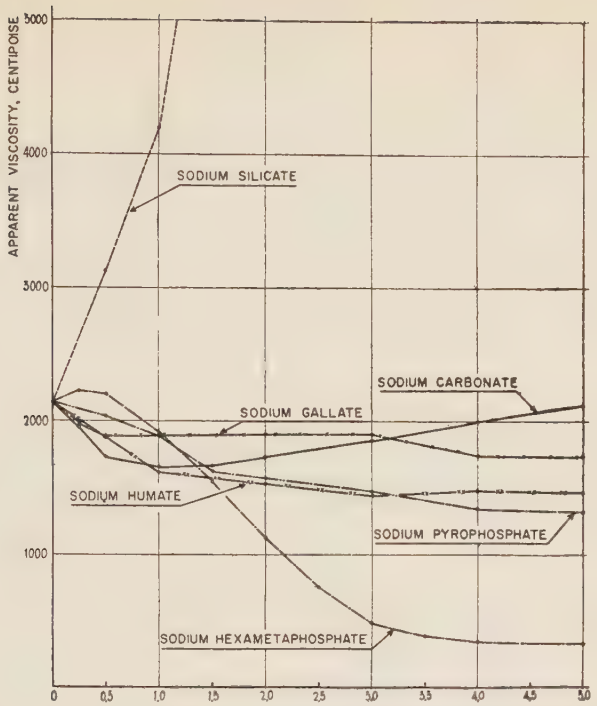
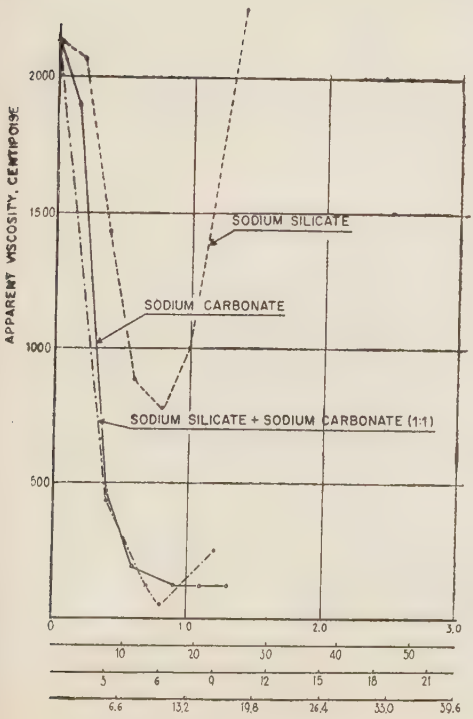


Figure 3. Effect of deflocculants on Clay No. 50 (unwashed)*



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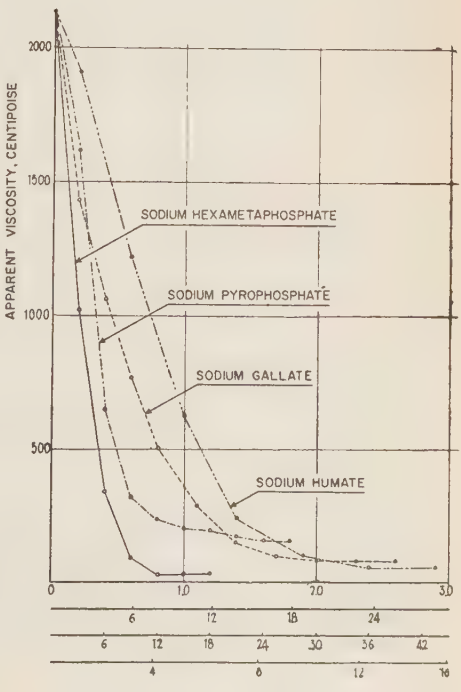

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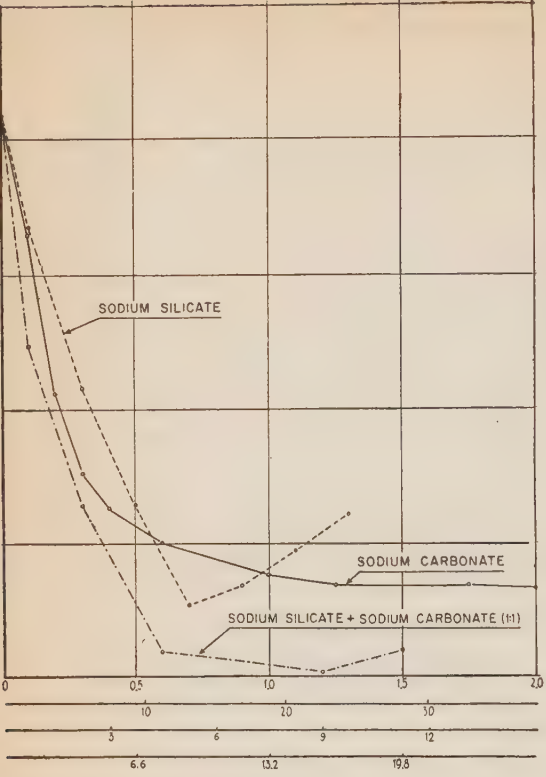

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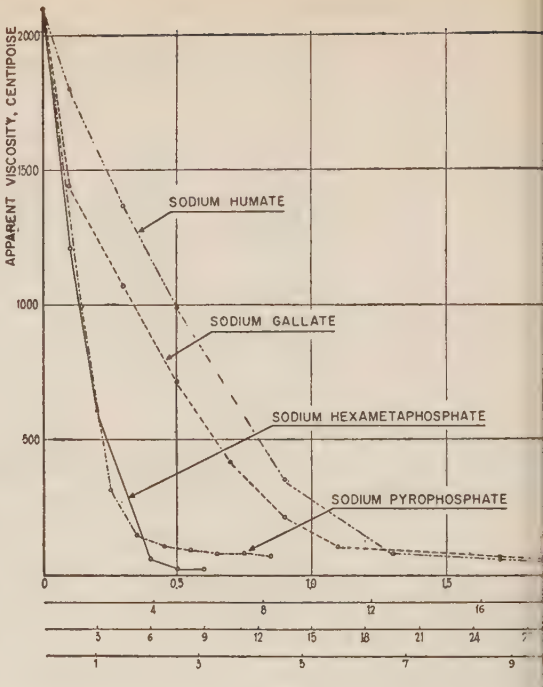

(b)

Figure 5. Effect of deflocculants on Clay No. 53

Key to figures:

In figures with four rows of abscissae, those in "a" figures (1a, 2a, 4a, 5a) represent respectively (reading from top to bottom): Per cent deflocculant (clay basis), meq sodium carbonate per 100 g clay, meq sodium silicate per 100 g clay, and meq of a 1:1 mixture of sodium silicate and sodium carbonate per 100 g clay; those in "b" figures (1b, 2b, 4b, 5b) represent: Per cent deflocculant (clay basis), meq sodium hexametaphosphate per 100 g clay, meq sodium pyrophosphate per 100 g clay, and meq sodium gallate per 100 g clay. In Figure 3, abscissa shows per cent deflocculant (clay basis).

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DETERMINATION OF QUARTZ IN LOCAL CLAYS BY MEANS OF X-RAY DIFFRACTION

D. Sternberg, J. Barta and B. Pratt
Technion – Israel Institute of Technology, Haifa

ABSTRACT

Determination of quartz in eight local clays was carried out by the X-ray diffraction method. A Geiger-Müller diffractometric technique with manual counting was used with calcium fluoride as internal standard, and a suitable calibration curve plotted. In order to obtain reproducible results, it was found necessary to reduce the samples to an average particle size of less than 5μ.

INTRODUCTION

The accurate determination of quartz in the presence of silicates and other minerals is a problem of particular importance in the ceramic and building industries, study and control of silicosis, and survey of clays and other mineral deposits.

There are several chemical methods for the determination of quartz. They are rather lengthy and sensitive to the details of operation; the results depend on the particle size of the quartz and cannot be applied uncritically to any material. As reported by Nagelschmidt[1], considerable discrepancies have been observed between the different methods, as well as between different laboratories using the same method. Chemical determination by the Shaw-Skinner method[1] showed an average error of about 4% of the amount present for samples containing 40–100% quartz, and an average error of 100% for samples containing 0–10% quartz.

Ballard (ref. 2, p. 422) and co-workers reported an analysis by the X-ray diffraction method of 19 mixtures containing 3.4–78.6% quartz, with an average error of about 7% of the amount present; in four samples, containing 0.59–2.1% quartz, the average error was as high as 16%. Clarke and Reynolds (ref. 2, p. 422) claim an accuracy of 5% of the amount present for a quartz content above 5%.

Klug[3] reports that with a recent-model diffractometer, manual counting and a calcium fluoride internal standard, accuracy up to 4% of the amount present can be obtained within the 10–100% content range.

THEORETICAL

If a monochromatic X-ray beam is allowed to impinge on a crystalline powder consisting of particles oriented at random, a diffraction pattern is obtained which

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can be intercepted either by a strip of photographic film (Debye-Scherrer method) or by a Geiger-Müller counter (diffractometric method). The pattern thus obtained is a characteristic of the substance analysed and can be used to identify its composition. In view of the distortion, due to absorption effects, of the linear relationship between the X-ray intensities and the amount present, indirect measurements must be resorted to. It was shown theoretically, and verified experimentally by Alexander and Klug[4], that when an internal standard is added in a constant proportion to the mixture analysed, the intensity ratio $I_{\text{ingredient}}/I_{\text{standard}}$ is proportional to the content of the ingredient obtained from a calibration curve prepared by means of a series of suitable intermediate mixtures of the pure ingredient and the standard. The intensities are read with the aid of a Geiger-Müller counter.

SAMPLES

The samples were provided by courtesy of Na'aman Works Ltd. and the Ceramic Research Association of Israel. Clays No. 50 and 53 were from the Wadi Hatira deposits and No. 1, S–5, S–6, flint clay and chocolate clay from Wadi Ramon.

The chemical analysis and properties of some of these clays have been described by Landsberg[5].

X-RAY EQUIPMENT

Philips X-ray generator PW/1010, with X-ray diffractometer PW/1050 and electronic circuit panel of diffractometer PW/1051, was used.

Operating conditions:

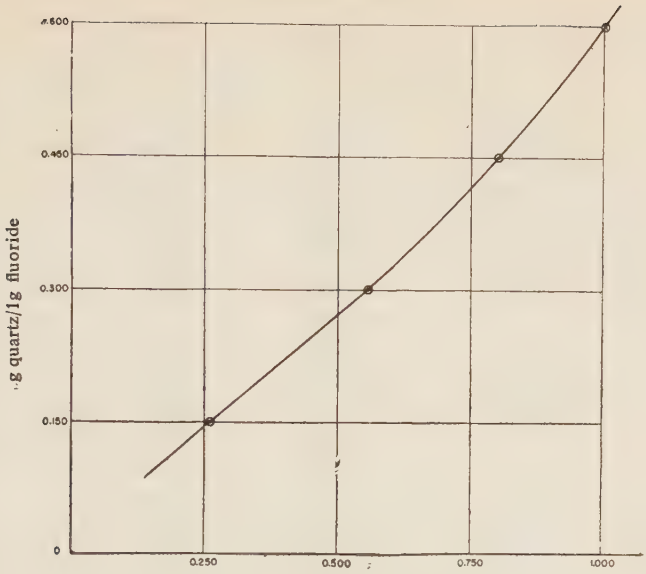
Cu target, Ni filter, 36 KV, 20 mA.

Slits: Divergence 1°
Scatter 1°
Receiving 1/15°, 0.2 mm.

EXPERIMENTAL PROCEDURE

Preparation of the calibration curve

The mixtures used in plotting the calibration curve were prepared from finely ground pure quartz (Ottawa sand), chemically precipitated calcium fluoride as internal standard, and calcite as diluent. It was shown by Klug and Alexander (ref. 2, p. 291) that in order to obtain a number of particles large enough to permit reproducible results, the average particle size should be less than 5μ, but above the limit at which the crystalline properties would disappear. The precipitated calcium fluoride was obtained fine enough for a high degree of reproducibility. The quartz and calcite were ground in a laboratory ball-mill and sifted through a 325-mesh sieve, and the undersize particles ($<45\mu$) re-ground in a Fisher motor-driven ("mullite") mortar grinder. After 6 hours of grinding, sedimentation and centrifugation tests showed that all material was below 5μ average size. Calcium fluoride and calcite were then



CALIBRATION CURVE
Figure 1

added in weighed amounts and blended for 4 hours in a Fisher ("minimill") laboratory ball-mill with porcelain balls, with methyl alcohol as dispersing agent.

The powder was placed in rectangular aluminium specimen holders by McCreery's technique (ref. 2, p. 300) so that a perfectly smooth and level surface was obtained. Three specimens were prepared from each mixture and 15 measurements of the 3.34Å quartz line ($2\Theta = 26.26°$) and of the 3.16Å fluoride line ($2\Theta = 28.25°$) were made, from which the calibration curve was plotted (see Figure 1 and Table I).

Analysis of the clays

The samples were ground in the ball-mill to pass through the 325-mesh sieve, and then for 6 hours in the "mullite" mortar grinder. The blending of the calcium fluoride standard with the clay samples was carried out as before. From each mixture two specimens were prepared and seven measurements of the 3.34Å and 3.16Å lines

TABLE I
Calibration curve mixtures

Mixture No.	Quartz (g)	Calcium fluoride (g)	Calcite (g)	I_q/I_f*
1	0.15	1.00	3.85	0.260
2	0.30	1.00	3.70	0.555
3	0.45	1.00	3.55	0.800
4	0.60	1.00	3.40	1.000

* I = intensity, q = quartz, f = fluoride

TABLE II

Quartz content of local clays

Sample	G clay / G fluoride	I_q* / I_f	G quartz / G fluoride	Free quartz (%)
Clay No. 1	2.3	0.690	0.375	16.3
	2.3	0.678	0.370	16.1
Clay No. 50	2.0	0.845	0.474	23.7
	2.0	0.885	0.504	25.2
Clay No. 53	2.3	0.718	0.396	17.2
	2.3	0.742	0.408	17.4
Clay S-5	2.0	0.941	0.552	27.6
	2.0	0.951	0.558	27.9
Clay S-6	2.0	0.885	0.508	25.4
	2.0	0.907	0.525	26.2
Chocolate Clay	2.3	0.889	0.508	22.1
	2.3	0.866	0.489	21.3
Ferrous Flint Clay "Pocket 2"	—	—	—	none
Flint Clay	—	—	—	none
White Flint Clay "Pocket 2"	—	—	—	none
Blue Base	—	—	—	none

* I = intensity, q = quartz, f = fluoride

taken for each specimen. From the average intensity ratio for each specimen, the amount of quartz per g fluoride was read from the calibration curve, and the percentage of free quartz in the sample calculated.

RESULTS

The experimental results, summarised in Table II, show that this method can be used for rapid and accurate analysis of a large number of samples of quartz mixtures.

The presence of free quartz in Clays No. 1, 50, 53, S-5, and S-6 confirms the hypothesis that these clays were formed by rapid sedimentation[6] while its absence in Flint Clay indicates either sedimentation or lateritisation. The lateritisation theory is commonly accepted[6].

The mineralogical composition of a clay is obtained from chemical analysis on the basis of the following assumptions[7]:

1. All alkalis are present as K_2O in microcline combined with the corresponding proportions of the total Al_2O_3 and SiO_2.

2. The entire remaining Al_2O_3 is combined with a proportion of the remaining silica and water to form kaolinite.

3. The remaining silica is free quartz.

Applying these assumptions to Clays No. 1, 50, 53, and flint clay studied here, the following results are obtained:

Clay	Free quartz, calc. (%)	Free quartz, X-ray method (%)
No. 1	14	16
No. 50	25	24.5
No. 53	19	17
Flint Clay	none	none

Considering the uncertainties involved in the above assumptions, the agreement between these results is satisfactory.

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EFFECTIVENESS OF SORBIC ACID IN INHIBITION OF MICROBIOLOGICAL SPOILAGE OF BREAD

Y. Pomeranz and L. Adler
Food Testing Laboratory, Ministry of Trade and Industry, Haifa

ABSTRACT

Levels of sorbic acid above 0.05% in flour are injurious to bread quality and loaf volume. This deleterious effect could not be overcome by increasing fermentation time as in the case of calcium propionate added at a 0.2% level to flour. Mixtures of sorbic acid and calcium propionate, at the levels employed, had a deteriorative effect on bread exceeding that of the sum of single adjuncts. The damaging effect of sorbic acid was more pronounced with dried than compressed yeast, and differences could be observed with the four brands of bakers' yeast tested.

Inhibition of mould growth on bread was effected by wrapping the loaves in paper treated with sorbic acid at levels ranging from 1.0 g to 5.0 g per 1000 sq. in., depending on the method of baking the bread. Calcium propionate added to the dough, at the 0.2% level, lowered the quantity of sorbic acid needed for extending the shelf life of wrapped bread.

Sorbic acid sprayed on boards used for storing bread was shown to be more than twice as effective in the prevention of mold growth on the bottom surface as calcium propionate.

Inhibition of ropiness in bread may now be regarded as a solved problem, but spoilage of bread by mould is still a question of interest and importance. Calcium propionate is effective in reducing mold growth to a certain extent, but for complete inhibition such concentrations are required as to have a detrimental effect on yeast activity and therefore on the volume and texture of the bread. A review of the literature and current studies concerning sorbic acid in foods point to its effectiveness as a fungistatic agent[1]. The use of sorbic acid seems especially promising in view of its reported harmlesness[4].

Sorbic acid on wrapping paper for general protection of foodstuffs is covered by a patent and has been described in the literature[2,6]. In an investigation on the fungistatic activity of sorbic acid relative to that of propionate in protection of cakes, sorbic acid was shown to be about four times as effective as propionic acid[4].

Rather extensive preliminary tests with sorbic acid added to dough in our laboratories showed that an addition of 0.1% (flour basis) prevented both mold and ropiness in bread. This concentration, however, cannot be applied practically, owing to its harmful effect on fermentation, bread volume and quality.

Since mold growth in bread normally starts on the surface, the effect of increasing the concentration of the fungistatic agent at the surface was investigated. This was

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accomplished by treating the wrapping paper and boards on which the unpacked bread was stored with a solution of sorbic acid.

MATERIALS AND METHODS

Bread composition and baking method

White bread was baked from a commercially milled, untreated bakers' straight flour, and brown bread from a high extraction wheat flour (Kent-Jones and Martin colour grade of 14°), with the addition of biologically inactive dry sour (Protosauer of the Diamalt A. G., Germany) and lactic acid. Both types of flour were milled from mixed grists of Hard Red Winter and Soft Red Winter wheat. Bread-baking methods employed, unless otherwise stated, were those given in Table I.

TABLE I

Bread composition and baking method

	White bread without Ca-propionate	White bread with 0.2% Ca-propionate	Brown bread
Flour (parts)	100	100	100
Yeast (parts)	3	3	1.5
Dry sour (parts)	—	—	6
Salt (parts)	1.3	1.3	2
Lactic acid (20% sol.) (parts)	—	—	1
Calcium propionate (parts)	—	0.2	—
Potassium bromate (gr/ton)	20	20	—
Water (parts)	59	59	71
Bulk fermentation (minutes)*	110	125	75
Proof (minutes)*	75	75	70
Fermentation temp. (°C)	30	30	30
Scaling weight (gr)	580	580	580
Baking temp. (°C)	210	210	210
Weight of bread (gr)	500	500	500

* Chosen so as to secure optimum conditions as judged by the operator

Compressed bakers' yeast was used, except where otherwise stated. Damage to yeast activity caused by fungistatic agents was tested with the following brands of commercial bakers' yeast: two samples of compressed yeast from local firms, active dried Standard Brands (Fleischmann, U. S. A.) and Engedura (Holland). The amount of dried yeast used was half the quantity of compressed yeast.

Preparation of wrappers

The inside surface of wax paper was sprayed with a 10% alcoholic solution of sorbic acid and was subsequently air dried. The quantities of sorbic acid applied

to the paper ranged between 0.5 g and 5.0 g of sorbic acid per 1000 sq. in., equivalent to 0.02–0.2% sorbic acid, based on bread weight.

Preparation of boards

Clean wooden boards, flushed with alcohol of 70% prior to treatment with the fungistatic agents tested, were divided into longitudinal strips, some of which were sprayed with a 10% alcoholic solution of sorbic acid at a rate of 2.5 g and some with a 20% water solution of calcium propionate at a rate of 5 g per 1000 sq. in.

Storage tests

Bread was kept for various periods up to 10 days in a cabinet maintained at a temperature of 30°C and relative humidity of 90% to 100%.

RESULTS AND DISCUSSION

The effect of sorbic acid added to flour on loaf volume and keeping quality of unwrapped pan loaves is summarised in Table II. Although special emphasis was placed on loaf volume as an index of bread quality, it was found generally that as the loaf volume decreased there was a corresponding reduction in other desirable qualities.

TABLE II

Effect of sorbic acid added to flour on loaf volume and protection against microbiological spoilage

Level of sorbic acid as % of flour	Loaf volume	Mold growth after		Ropy spoilage after	
		5 days	7 days	5 days	7 days
			White pan bread		
—	1875	+++	++++	++	++++
0.050	1850	++	+++	+	++
0.075	1650	—	—	—	+
0.10	1375	—	—	—	—
0.20	1300	—	—	—	—
0.40	1175	—	—	—	—
			Brown pan bread		
—	1100	+++	++++	—	—
0.050	1075			—	—
0.075	1062			—	—
0.10	1012	—	—	—	—
0.25	950	—	—	—	—

In a second series of experiments, an attempt was made to diminish the deleterious effect of sorbic acid on yeast activity by lengthening fermentation time. Addition of 0.2% calcium propionate generally necessitated about 20% longer fermentation time. The effect of changing fermentation times of doughs containing sorbic acid is shown in Table III.

TABLE III

Effect of changing fermentation time—in presence of sorbic acid—on loaf volume of white pan bread

Level of sorbic acid as % of flour	Bulk fermentation (min)	Proof (min)	Loaf volume (cc)
—	105	60	1937
—	105	75	1875
0.05	125	65	1812
0.05	125	75	1850
0.075	125	75	1650
0.075	125	90	1700
0.10	125	75	1375
0.10	125	100	1550

Whereas optimum bread was obtained in control tests after 165 min total fermentation time, increase of about 40% fermentation time at 0.1% sorbic acid addition did not prevent the damaging effect on loaf volume and overall characteristics. A level of 0.1% sorbic acid proved to be the safe minimum for protection against mold.

Repetitions of the test showed conclusively that levels of sorbic acid above 0.05% in flour are injurious to bread quality and loaf volume. These findings are in agreement with results published after completion of our experiments[3].

Raible and Bush showed that on using sorbic acid alone and in combination with boric acid no synergistic effect was noted[5].

The effect of adding various fungistatic agents, alone and mixed, on loaf volume, tested on 4 brands of active yeast, is given in Table IV.

TABLE IV

Bread volume decrease as percentage of control caused by various fungistatic agents to different yeast brands

Fungistatic agents				*% of flour*				
Calcium propionate	—	0.13	—	0.2	—	—	0.13	—
Calcium acetate	0.2	—	0.3	—	—	0.2	—	—
Sorbic acid	—	—	—	—	0.03	0.03	0.03	0.05
Yeast brand				*% bread volume decrease*				
Dried yeast A	1.2	7.4	7.4	16.1	8.6	8.6	19.8	16.1
Dried yeast B	3.9	13.0	7.8	24.7	7.8	15.6	28.7	16.9
Compr. yeast A	—	−1.3	3.9	1.3	1.3	1.9	3.2	3.9
Compr. yeast B	−1.4	−6.7	3.0	−1.4	1.4	—	1.4	2.6

Results of tests on various brands of bakers' yeast show that active dried yeast was more susceptible to damage than compressed yeast. The damage to loaf volume caused by fungistatic agents used singly was small. However, with both compressed

and dried yeast, mixtures of these agents caused what appeared to be a synergistic effect. Thus, for example, a mixture of 0.03% sorbic and 0.13% calcium propionate produced a loss in loaf volume greater than the sum of the effects of these agents used individually.

In view of the variations in receptibility observed with different yeast brands, the possibility of selecting or "adapting" yeast strains with lowered susceptibility seems feasible.

The effect of treatment of waxed wrapping paper with sorbic acid is shown in Table V. Cut surfaces, fortuitously contaminated with mold spores, showed fungal growth starting from inside the sliced bread, with a reduction in effectiveness of spoilage inhibition when wrappers were sprayed with sorbic acid.

TABLE V

Effect of sorbic acid incorporated into wrapping paper on rope and mold spoilage

Loaf no.	Level of sorbic acid in wrapper (gr/1000 sq. in.)	Kind and degree of deterioration		
		Rope in unsliced bread	Mold in unsliced bread	Mold in sliced bread
		White bread without Ca-propionate		
1	—	++++	++++	++++
2	0.5	++++	+++	
3	1.0	+++	++	+++
4	2.5	+++	—	+++
		White bread with 0.2% Ca-propionate (flour basis)		
5	—	—	+++	+++
6	0.5	—	++	
7	1.0	—	—	+**
8	2.5	—	—	+**
		Brown bread with dry sour and lactic acid		
9	—	—*	++++	++++
10	1.0	—	—	++
11	2.5	—	—	+++
12	5.0	—	—	+**

* No spoilage due to rope was observed in brown bread as growth of *Bacillus mesentericus* was inhibited by acidity

** No fungal growth was observed on the crust; the spoilage was found to start from the interior surface of the slices only

Results in Table V show that the addition of calcium propionate to the flour at the level employed not only protected the bread against ropy spoilage, but also substantially lowered the amount of sorbic acid needed for impregnation of wrappers, as may be seen from Figure 1.

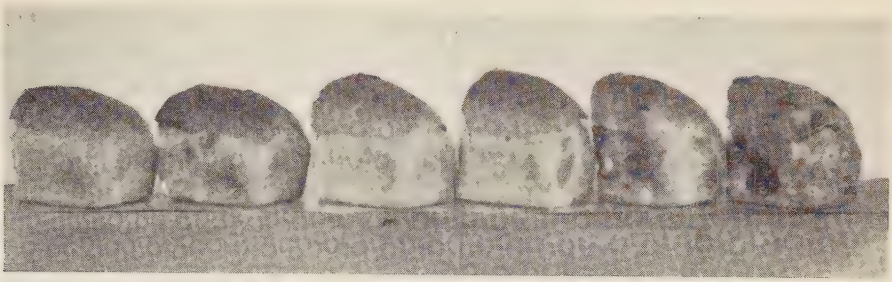

Figure 1
Effect of calcium propionate added to flour and sorbic acid to wrappers on mold growth on unsliced bread. Right to left: loaves No. 1, 2, 3, 4, 6, 7 (see Table V)

At the effective levels of sorbic acid no objectionable taste, smell, or change in color of crumb or crust were observed.

Brown bread placed on a wooden board half of which was treated with sorbic acid showed, after 10 days' storage at room temperature, pronounced mold growth on the untreated part and fungal inhibition on the bottom surface of the loaf in contact with the treated part. Figure 2 shows the bottom surface of some of the loaves, with fungal growth on the part stored on untreated board and no signs of attack on the part stored on the treated strip.

In order to assess the relative effectiveness of sorbic acid and calcium propionate, boards were divided longitudinally into three parts, and while the middle part was left untreated, the outer parts were sprayed with sorbic acid and calcium propionate respectively.

Ten loaves of either white or brown pan bread were placed on a board and kept for 10 days in a cabinet at 30°C and 90–100% R.H.

Figure 2
Inhibition of fungal growth on bottom surface of bread. Lower part stored on sorbic acid-treated board, upper part stored on untreated board

The part of the bread kept on the untreated board showed in all cases, on examination after 10 days, strong fungal growth. The attacking mold cultures consisted of the common air-borne molds associated with fungal bread spoilage and included species of *Aspergillus* (mainly an unidentified species of the *Aspergillus glaucus* group and *Aspergillus niger*), *Penicillium*, and *Rhizopus*.

At the levels of fungistatic agents employed (ratio of sorbic acid to calcium propionate 1:2) none of the brown bread kept on the sorbic acid-treated strip showed fungal growth, and on two of the white loaves isolated colonies of *Aspergillia* were found. With loaf parts kept on calcium propionate-treated boards, fungal growth was found in one case on brown bread and in 6 cases on white bread. Sorbic acid proved more than twice as effective as calcium propionate in the inhibition of fungal growth under the test conditions employed.

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STORAGE STABILITY OF THERMALLY-REFORMED MOTOR-TRANSPORT GASOLINE

A. B. Stern
Ministry of Defence
AND
M. Babitz
Fuel Testing Laboratory, Technion – Israel Institute of Technology, Haifa

ABSTRACT

The influence of prolonged storage on the chemical and physical properties of a straight-run gasoline and a thermal reformate of 79 octane (research method) was studied. Both gasolines were leaded and inhibited with an amine-type anti-oxidant inhibitor; the reformate was inhibited with varying amounts. The properties of the straight-run gasoline remained almost unchanged, whereas the reformate gradually increased in gum content and decreased in oxidation stability. An inhibitor concentration of about 80 ppm seems to be the most beneficial amount to keep the reformate within specification limits.

INTRODUCTION

The object of this study was to investigate the practicability of prolonged storage of commercial thermally-reformed gasoline of 79 octane (research method), refined at Haifa's Consolidated Refineries Ltd. Under normal conditions this gasoline is not stored for periods longer than a few weeks, and thus has not given rise to any performance troubles.

The reformed gasoline is inhibited with an anti-oxidant inhibitor at the refinery, with the object of reducing gum formation to a minimum. The added quantities are of such an order as to guarantee a gum content and oxidation stability[1,2] in compliance with the current Israel Standard No. 90, 1956: Hydrocarbon Fuels—Motor Transport Benzine[8], i.e. normal-grade gasoline without any special requirements as to stability on prolonged storage.

In the course of this study, a straight-run gasoline was compared with the reformed gasoline, both leaded to the same level. The latter was a commercial gasoline blended with varying amounts of antioxidant inhibitor, in order to investigate the effectiveness of the inhibitor in improving the storage stability of the gasoline.

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Deterioration of gasoline on storage

The incidence and extent of gasoline deterioration on storage depends mainly on its type and composition, and to a certain degree also on the type of container, climatic conditions and other factors.

The various factors or phenomena affecting the quality of gasoline are as follows:

1. Weathering[5,15].
2. Contamination[10,15].
3. Colour fading and lead precipitation[7,9,12,15].
4. Gum formation and oxidation stability[4–7,9,13–15].

Any of these may result in a fuel failing to meet the specification.

PROCEDURE

The two gasolines studied were a thermally-reformed 79 octane (research method) with a lead content of 1.8 ml/IG and a straight-run cut with the same lead content and an octane number of 79 (motor method). Both were inhibited with the same approved anti-oxidant inhibitors, namely N,N′-di-*sec*-butyl-*p*-phenylene-diamine, the reformed fuel being inhibited with varying amounts. A master solution of the inhibitor was prepared, and aliquot quantities were added to the gasoline.

The gasolines were stored in clean commercial 210-litre steel drums, provided with two openings, $^3/_4''$ and 2″ Trisure closure, at one end. The drums were placed in a vertical position with the openings up.

The drums, each containing about 200 litres of gasoline, were marked as follows:

"A" — reformed gasoline, inhibitor content 30 ppm
"B" — reformed gasoline, inhibitor content 50 ppm
"C" — reformed gasoline, inhibitor content 80 ppm
"D" — straight-run gasoline, inhibitor content 20 ppm.

The drums were kept uncovered in the open courtyard of the Petroleum Testing Laboratory for one year. Fortnightly temperature readings were taken, and 2-litre samples periodically drawn through the 2″ opening with the aid of a glass hand-pump. After the sample had been drawn, the rubber washers of the closures were replaced by new ones and the bungs tightly re-sealed.

RESULTS

The results are summarised in Table I. All physical and chemical properties of the various samples were determined by the appropriate I.P. or A.S.T.M. methods[1,2] unless otherwise stated.

The increase in gum content is one of the most critical factors in stored gasoline. For this reason two gum determinations were carried out for each sample, namely, the I.P. glass-dish gum (IP–38), followed by the *n*-heptane insolubles, and the more rigorous copper-dish gum (U.S. Standard VV-L-79b). In addition to the routine tests, all samples were tested for corrosive sulphur (ASTM D-130-Sulfur (Corrosive) in Motor Fuels, 3 hours at 100°C), peroxide value and bromine number.

	Original reformate	Reformate with 30 ppm inhibit				
Date of sampling	26.4.56	A1 15.5.56	A2 15.6.56	A3 15.7.56	A5 16.9.56	A8 19.1
Density at 15°C	0.7320	0.7332	0.7340	0.7342	0.7343	0.733
Distillation						
I.B.P. °C	38	39	40	40	40	38
10%	60	62	63	64	61	63
20%	73	75	75	77	74	76
30%	86	88	88	89	87	88
40%	98	100	100	101	98	100
50%	110	111	111	112	110	111
60%	121	123	122	123	121	122
70%	134	134	133	133	133	132
80%	148	148	148	144	142	147
90%	166	166	165	166	166	165
F.B.P.	190	186	189	191	188	189
Corrosion, copper-strip						
3 hours at 50°C	1	1	1	1	1	1
3 hours at 100°C	9	9	9	9	9	9
Total sulphur, %wt	0.09					
Reid vapour pressure, psi	8.2					
Existent gum						
IP-glass-dish, mg/100 ml	1.2	4.8	5.0	5.6	6.5	9.0
n-Heptane insolubles, mg/100 ml			3.0	5.0	5.0	6.6
Existent gum, copper-dish						
mg/100 ml		4.7	4.0	5.6	7.1	10.2
Oxidation stability, min		360	315	310	285	25
T.E.L. content, ml/IG	1.77				1.76	
Octane number CFRM, F-1	79				78	
Bromine number		33.4	33.0	34.4	33.4	33
Peroxides, mg O_2/litre				1.9	1.9	2.3
Potential gum — IP after 5 hours oxidation						
Peroxides of the oxidised gasoline, mg O_2/litre						

TABLE I

Prolonged storage of thermally-reformed gasoline and straight-run gasoline

or		Reformate with 50 ppm inhibitor						Reformate wi		
2.56	A13 15.5.57	B1 15.5.56	B2 15.6.56	B3 15.7.56	B5 16.9.56	B8 19.12.57	B13 15.5.57	C1 15.5.56	C2 15.6.56	C3 15.7
39	0.7344	0.7344	0.7339	0.7341	0.7341	0.7337	0.7344	0.7335	0.7332	0.73
3	40	39	41	39	40	33	41	37	39	4
3	62	61	63	63	65	59	62	58	63	6
5	74	75	76	76	77	72	73	71	77	7
3	86	88	89	88	90	84	85	84	89	8
0	98	100	100	100	101	96	97	96	011	10
	110	111	112	111	112	108	109	108	112	11
2	121	123	122	122	123	121	120	119	123	12
2	132	134	133	133	135	132	131	131	133	13
7	145	148	142	146	147	146	144	145	145	14
5	163	166	165	165	167	164	162	162	167	16
9	188	186	189	189	191	188	187	185	190	19
	1	1	1	1	1	1	1	1	1	1
	9	9	9	9	9	9	9	9	9	9
	12.8	4.7	4.8	5.0	4.9	7.0	9.5	4.3	4.0	4.0
	8.2		2.3	3.5	3.0	5.0	7.5		2.9	3.5
2	11.8	4.9	6.0	6.0	6.0	8.0	8.0	3.3	3.8	5.6
5	285	375	390	395	360	350	360		615	60
	1.73						1.75			
	78						79			
2	33.1	34.0	34.5	34.0	34.0	33.7	34.4	34.4	34.5	33
	2.3			1.9	1.9	2.3	2.7			1.
	217									
	77.5									

ppm inhibitor			Original straight-run cut	Straight-run cut with 20 ppm inhibitor					
C5 6.9.56	C8 19.12.56	C13 15.5.57	 9.3.56	D1 15.5.56	D2 15.6.56	D3 15.7.56	D5 16.9.56	D8 19.12.56	D13 15.5.57
.7340	0.7333	0.7340	0.7302	0.7306	0.7313	0.7320	0.7320	0.7318	0.7330
40	35	41	42	42	47	43	47	48	50
63	60	62	68	68	70	68	70	72	72
75	74	74	78	78	80	78	80	82	81
87	86	85	87	87	89	87	89	89	89
100	98	97	96	96	96	95	96	96	96
111	109	109	104	103	103	102	104	104	104
121	121	120	110	109	110	109	111	110	110
133	133	131	118	116	117	116	118	117	117
146	144	145	127	124	125	124	127	125	123
165	165	161	138	135	136	135	137	136	135
188	188	187	160	160	161	160	160	159	159
1	1	1	0	0	0	0	0	0	0
9	9	9	0	0	0	0	0	0	0
			0.01						
			6.2						
5.0	6.2	8.0	1	4.2	4.8	4.1	4.0	4.0	4.0
3.5	3.6	5.2		2.0	2.4	2.0	2.0	1.5	2.0
5.0	7.2	6.1		4.1	4.1	4.5	4.5	5.0	5.0
585	615	645	1440+	1440+	1440+	1440+	1440+	1440+	1440+
1.76		1.80		1.80					1.94
79		79.5		78					79
34.2	33.6	34.2		0.5	0.5	0.4	0.4	0.5	1.0
	2.3	2.3		0	0	0	0	0	0
		20							5.8
		10.9							10.9 after 16 hrs oxidation

Figures 1–4 give the increase in gum and *n*-heptane insolubles.

Figure 5 gives the changes in oxidation stability of the reformed gasolines A, B and C.

Figure 6 shows the influence of different anti-oxidant concentrations on 6 mg/100 ml gum time (i.e. the appropriate oxidation stability in minutes, at 6 mg/100 ml I.P. glass-dish gum).

Figure 7 gives the average temperature readings over the test period, as well as the maximum and minimum.

Visually, the gasolines did not undergo any change in appearance and retained their characteristic smell. Colour did not fade, and no precipitation could be observed.

In all cases density increased very slightly, due to evaporation of some of the lighter constituents, which also affected the distillation. The straight-run gasoline showed somewhat stronger weathering due to its original lighter composition.

No change in copper-strip corrosivity was observed; the 3-hour test at 50°C remained well within specification limits and not more than No. 1 by the Indiana scale[11], although the Airwell method[12] gave high figures from the outset (No. 9 by the Indiana scale). The latter method (3 hours at 100°C) is not prescribed for MT gasolines and was only used for purposes of comparison and control. It is interesting to note that some gasolines can be sweetened by the diamine anti-oxidant, which causes mercaptane conversion and in some cases reduces the corrosivity[7]. As in the present case the corrosivity at 100°C did not change during the whole period of storage, it may be concluded either that free sulphur, not mercaptanes, is the predominant factor in causing corrosion or that, assuming the mercaptanes are the active constituent in causing corrosion, they are not affected by the inhibitor.

The total sulphur content of the reformed gasoline was higher than that of the straight-run fuel, which may have some bearing on the corrosion results.

As already mentioned, the most critical factor in reformed gasolines in storage is the tendency towards gum formation. The gum content increases gradually, finally reaching a prohibitive level which renders the gasoline unsuitable for use. The IP glass-dish results are shown in the various graphs with the permissible maximum, 6 mg/100 ml, indicated by a horizontal line, from which the maximum permissible storage period can be read. The copper-dish gum results vary slightly, compared with the IP gums, but generally tend to be higher. In this study the differences between glass- and copper-dish gums were actually small, demonstrating the high effectiveness of the inhibitor used.

In the reformed gasolines, the increase in gum content was rapid at the beginning of the storage period. The greatest increase was exhibited by gasoline "A", the fuel with the lowest inhibitor content, and the least increase by gasoline "C", with the highest inhibitor content. Figure 6 shows the improvement in oxidation stability with increasing inhibitor concentration.

In contrast to the reformed gasoline, the straight-run product remained stable and unchanged over the storage period. The relatively great increase in gum content

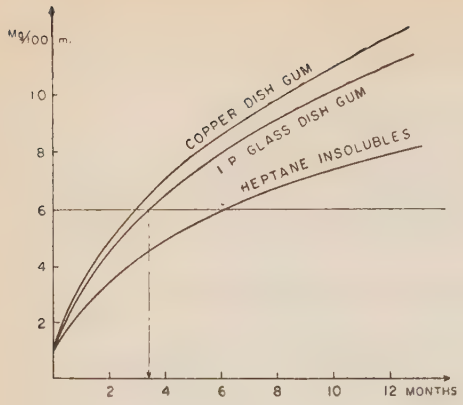

Figure 1
Gum content vs. storage time — gasoline A

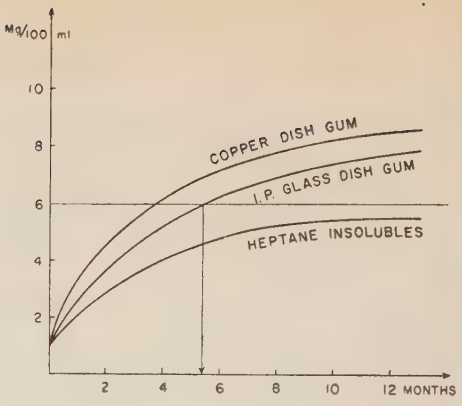

Figure 2
Gum content vs. storage time — gasoline B

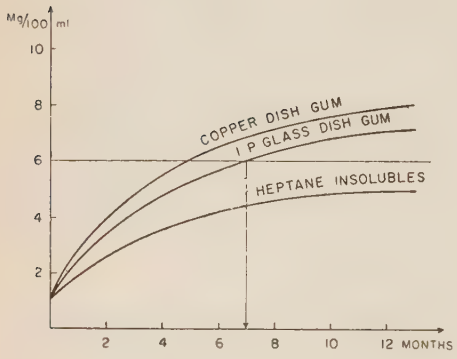

Figure 3
Gum content vs. storage time — gasoline C

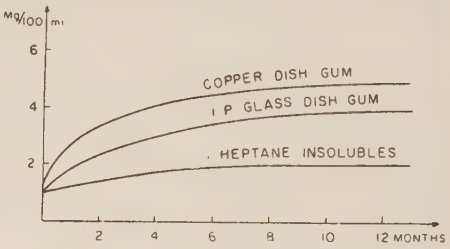

Figure 4
Gum content vs. storage time — gasoline D

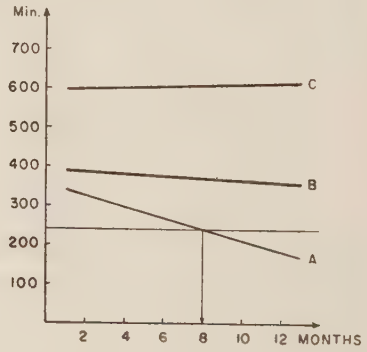

Figure 5
Oxidation stability vs. storage time

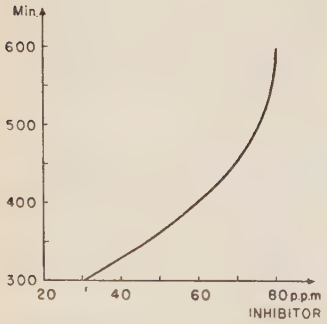

Figure 6
Oxidation stability vs. inhibitor concentration (6 mg/100 ml gum time, gasolines A, B, C)

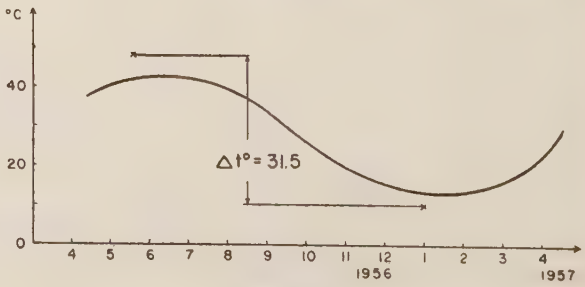

Figure 7
Average temperatures (gasolines A, B, C, D)

in gasoline "D" over one month of storage should be ascribed to contamination of the gasoline by impurities in the drum, but once the higher value was reached no further increase was observed.

The curve of *n*-heptane insolubles is much flatter than that of the IP gum. These insolubles may be considered as a harder, more polymerised fraction of the gum. They provide a certain indication of the extent and mechanism of gum formation, and a more detailed investigation may show that the ratio of IP gum and *n*-heptane insolubles may serve as an index of stability for certain gasolines and a means of control in the reforming operation.

It may be noted that the reformed gasoline inhibited with 30 ppm anti-oxidant reached the maximum permissible 6 mg/100 ml IP glass-dish gum after about 4 months of storage. Addition of 20 ppm increased this period to about 6 months, but a further addition of 50 ppm only increased it by one more month. The comparatively moderate climatic conditions of Haifa must, however, be borne in mind. On prolonged storage in the hotter regions of the country the rate of gum increase would be more rapid.

The generally accepted civilian and military specification limits with regard to gum content and oxidation stability are as follows:

IP gum, mg/100 ml	4–10
ASTM gum, mg/100 ml	4–7
Oxidation stability, minutes	
Ordinary	200–240
For prolonged storage	360–480

In conjunction with the gum content, peroxide values were determined by the iodometric method, IP–30. No appreciable increase could be found, the values for the reformed gasolines varying from 1.9 mg oxygen per litre gasoline to about 2.5 mg, while the straight-run cut remained peroxide-free throughout the whole storage period.

In a later oxidation stability test after 13 months' storage in which the gasoline was oxidised for 5 hours (potential gum determination), the IP gum for the oxidised gasoline "A" was 217, for "C" 20, and for "D" 5.8 mg/100 ml gum. Peroxide values of 77.5 for gasoline "A" and 10.9 for gasoline "C" were found. Gasoline "D" was oxidised for 16 hours with the result of 11.0 mg peroxide oxygen per litre gasoline. This rigorous test is further proof of the high effectiveness of the anti-oxidant inhibitor and of the relationship between the gum content and peroxide value.

CONCLUSION

It has been confirmed that straight-run gasoline does not deteriorate on prolonged storage, whereas thermally-reformed gasoline tends to gum formation, although remaining well within specification limits in respect of other properties.

There is no special requirement in current Israel specifications for a safe storage period apart from the oxidation stability limits, which do not give a definite indication

of this period; it may be assumed that normally-reformed gasoline will remain within specification limits up to 4 months.

It has also been confirmed that increasing amounts of an approved amine-type anti-oxidant inhibitor improve storage stability and retard gum formation. This type of anti-oxidant, at a concentration of 80 ppm, is highly effective and ensures the maximum of 6 mg/100 ml gum in 6–8 months of storage. The *n*-heptane insolubles following the IP gum test may provide indications of the mechanism of gum-formation and data for evaluation of the gasoline.

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A STEEL BEAM ON IMMOVABLE SUPPORTS

A. ZASLAVSKY

Division of Structural Engineering, Technion – Israel Institute of Technology, Haifa

ABSTRACT

In a simply supported beam one support is assumed to be movable. The movability of the support prevents the appearance of additional stresses due to axial forces induced by temperature, second-order deformations, etc.; also no horizontal forces are transmitted to the supporting columns, etc.

This paper deals with a single-span steel beam supported by two absolutely immovable supports under normal loading. It is shown that a considerable *compressive* axial force is induced in the beam, and the stresses are calculated.

Let us first consider an ordinary beam AB (Figure 1) subjected to a load P at mid-span. Assuming the supports to be at the level of the neutral axis, the movable support B will move to the left for the distance

$$\Delta n = 2\int_o^{l/2}(ds - dx) \cong \int_o^{l/2}\left(\frac{dy}{dx}\right)^2 dx \tag{1}$$

Considering the equation of the elastic line for the beam:

$$y = \frac{Pl^3}{16EI}\left(\frac{x}{l} - \frac{4x^3}{3l^3}\right) = 3f\left(\frac{x}{l} - \frac{4x^3}{3l^3}\right)$$

$$\left(\frac{dy}{dx}\right)^2 = \left[\frac{3f}{l}\left(1 - \frac{4x^2}{l^2}\right)\right]^2$$

$$\Delta n = \int_o^{l/2}\left[\frac{9f^2}{l^2}\left(1 + \frac{16x^4}{4l^2} - \frac{8x^2}{l^2}\right)dx\right] = 2.4\frac{f}{l} \tag{2}$$

(f = the maximum deflection at midspan).

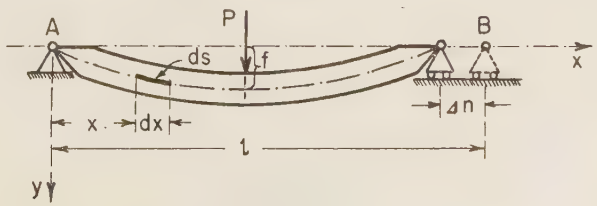

Figure 1

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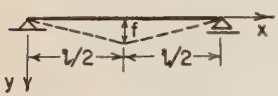
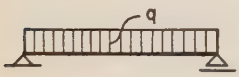
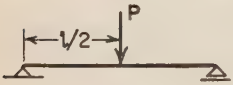
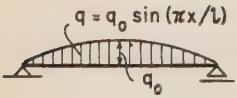
In the following table the results for Δn are given for different loading cases as calculated by Eq. (1). The first case is a theoretical minimum case for a triangular elastic line.

TABLE I
Shortening of the span Δn

Case	Elastic line	Δn
	Triangle (theoretical limiting case)	$2.0\frac{f^2}{l}$
	$F(x, x^3, x^4)$	$2.15\frac{f^2}{l}$
	$F(x,\ x^3)$	$2.4\frac{f^2}{l}$
	$F(\sin\ x)$	$2.47\frac{f^2}{l}$
	Parabola (circle)	$2.67\frac{f^2}{l}$

Now we find the elongation Δl of the bottom fibre (Figure 2; y = axis of symmetry; l = length of neutral line):

$$\Delta l = \int_o^l \varepsilon_1\, dx = \int_o^l \frac{\sigma_1}{E}\, dx = \int_o^l \frac{Mh_1}{EI}\, dx = \frac{h_1}{EI}\int_o^l M\, dx = \frac{h_1}{EI}\, A_M \qquad (3)$$

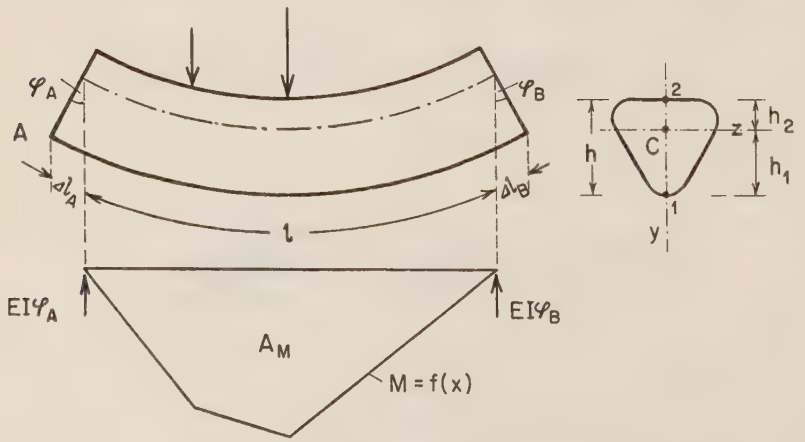


Figure 2

The integral represents the bending moment area A_M and the result may be deduced directly by considering Figure 2:

$$\Delta l = \Delta l_A + \Delta l_B = h_1 (\varphi_A + \varphi_B) = \frac{h_1}{EI} A_M$$

For sections with two axes of symmetry:

$$\Delta l_A = \frac{h}{2EI} A_M \tag{4}$$

For the case shown in Figure 1 ($f = Pl^3/48EI$):

$$\Delta l = \frac{Pl^2 h}{16EI} = 3f \frac{h}{l} \tag{5}$$

Considering (2):

$$\Delta l = 1.25\, \Delta n \frac{h}{f} \gg \Delta n \tag{6}$$

i.e. the elongation (Δl) of the bottom fibre is much larger than the shortening (Δn) of the span and therefore the support B will move to the *right*, since—as a rule—the support is fixed to the bottom of the beam.

While Δn may be regarded as a second-order deformation, this is not the case with Δl and we may neglect Δn as against Δl. To simplify the analysis, let us assume an I-beam so designed that both the admissible stress and the admissible deflection are utilised simultaneously:

$$\left.\begin{aligned} \sigma_{adm} &= \pm\ 1400\ \text{kg/cm}^2 \\ f &= l/400 \end{aligned}\right\} \tag{7}$$

$$f = \frac{Pl^3}{48EI} = \frac{\sigma_{adm} l^2}{6Eh} = \frac{l}{400}$$

$$h = \frac{67\, \sigma_{adm} l}{E} = \frac{l}{22.5} \tag{8}$$

($E = 2.1 \times 10^6$ kg/cm^2, Young's modulus).

Furthermore, by virtue of Eqs. (2), (5) and (8):

$$\Delta l = \frac{\sigma_{adm} l}{2E} = \frac{f}{7.5} \tag{5a}$$

$$\Delta n = \frac{\Delta l}{22.2} = \frac{\sigma_{adm} l}{44.4\, E} = \frac{f}{167} \tag{6a}$$

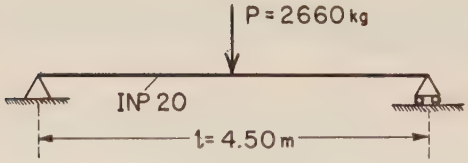


Figure 3

As an illustrative example, consider an I-beam No. 20 according to Figure 3:

$$f = 4500/400 = 11.25 \text{ mm}$$
$$\Delta l = 11.25/7.5 = 1.5 \text{ mm}$$
$$\Delta n = 11.25/167 = 0.07 \text{ mm}$$

Now we take the case when both supports are absolutely immovable (Figure 4). Again neglecting Δn as well as the small change in the bending moments due to the elastic line of the beam, we obtain the horizontal force H from the condition:

$$\Delta l_M - \frac{Hl}{EA} = 0; \; h\varphi_A - \frac{Hl}{EA} = 0 \tag{9}$$

$$\frac{h}{EI}\left[\frac{Pl^2}{16} - \frac{Hhl}{4}\right] - \frac{Hl}{EA} = 0$$

$$H = \frac{Plh}{4h^2 + 16I/A} = \frac{Pl}{4h + 8Z/A} \tag{9a}$$

(Z = section modulus).
In our numerical example:

$$H = \frac{2660 \times 450}{4 \times 20 + 8 \times 214/33.5} = \frac{1{,}197{,}000}{80 + 51} \cong 9150 \text{ kg} \cong 3.44P$$

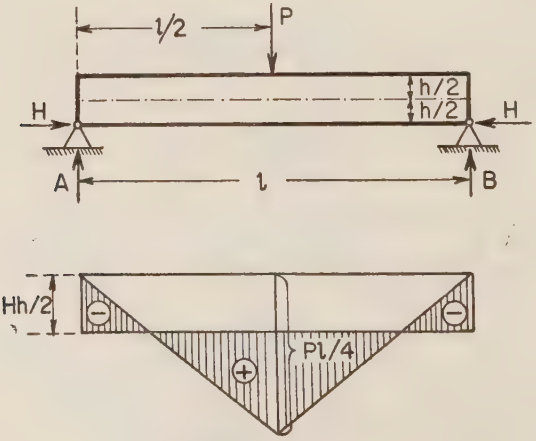


Figure 4

The force H reduces the maximum compressive stress at the top fibre:

$$\begin{aligned} -M_P/Z = 2660 \times 450/(4 \times 214) &= -1400 \\ -M_H/Z = 9150 \times 10/214 &= +430 \\ -H/A = 9150/33.5 &= -270 \\ &\overline{-1240 \text{ kg/cm}^2} \end{aligned}$$

But if no adequate transverse bracing is provided, the buckling danger is quite considerable. (However, after buckling has set in the force H diminishes and there is no danger of progressive buckling).

Assuming a change of *temperature* of $+ t°$, the force H may be calculated from Eq. (9a) after adding the thermal elongation $\alpha t l$ to Δl_M. In this case H is larger:

$$H = \frac{Pl + 16\, EI\alpha t/h}{4h + 8Z/A} \tag{10}$$

For $t = 20°$ the theoretical result is $H = 22400$ kg (instead of 9150 kg).

For a beam under *uniformly* distributed load $Q = ql$ we obtain similarly:

$$H = \frac{Ql}{6h + 12Z/A} \tag{11}$$

Equations (9)–(11) may also be derived by Castigliano's theorem of least work: $\partial U/\partial H = 0$.

CONCLUSION

The behaviour of the beam under discussion is analogous to that of a hinged portal frame with very short legs (Figure 5). Although in practice there are no absolutely rigid supports, the paper demonstrates that a considerable undesirable compressive axial force may be induced. Similar considerations apply to continuous beams.

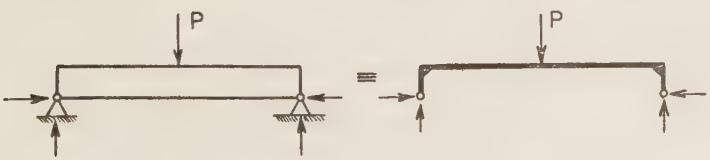


Figure 5

STATISTICAL METHODS IN THE EVALUATION OF THE TIMNAH COPPER DEPOSIT

N. SOFFER
Israel Mining Industries Laboratories, Haifa
AND
P. NAOR
Technion–Israel Institute of Technology, Haifa

ABSTRACT

The Timnah copper ore deposit is examined by the technique of analysis of variance. The region of the deposit is recognized to be heterogeneous with respect to average copper content and a partitioning scheme is indicated which defines relatively homogeneous subregions. The underlying assumptions of the statistical model are reviewed in detail and the adopted procedures are clarified. Confidence limits for the average copper percentage are calculated which may provide some assistance in setting up a mining plan.

1. INTRODUCTION

The exploration of an area for mineral content is a costly operation. It seems worthwhile, therefore, to put to maximum use the data obtained relating to quantities, percentages, quality and other characteristics of the mineral. It would appear that the most reasonable and at the same time most reliable approach to proper evaluation utilizes the tools of modern applied statistics.

This study is concerned with the statistical analysis of exploration data and the estimation of copper content in various regions of a copper-bearing deposit.

The copper deposit whose investigation is reported here is situated in the extreme southern part of Israel that ends on the northern shores of the Red Sea about 180 kilometres south of the Dead Sea.

The exploration results known to date show that the copper-bearing rock covers an area in the shape of a triangle of about two square kilometres in the Timnah Wadi, which is an eroded semi-circular valley[1]. The copper ore outcrops after removing a layer of gravel of several metres' thickness at the northern boundary of the deposit, which forms the base of the triangle. The ore body possesses an average thickness of 6 metres and dips downwards in a somewhat irregular manner in a southerly direction; it is found at a depth of 200 metres in the farthest bore-hole to the south. Faulting can be seen at the outcrop area and evidently the ore body is faulted in other parts as well, and its thickness is extremely variable.

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The copper occurs in an oxidized form, and no sulphide mineralization was found in the ore body or its vicinity. Manganese is the only mineralization other than copper found in the ore body itself.

No ready and easily obtainable evidence exists for tracing the origin of the copper ore or its parent mineral. The rock consists mainly of sandstone and it seems that part of the copper mineral forms a cement binding sandstone grains.

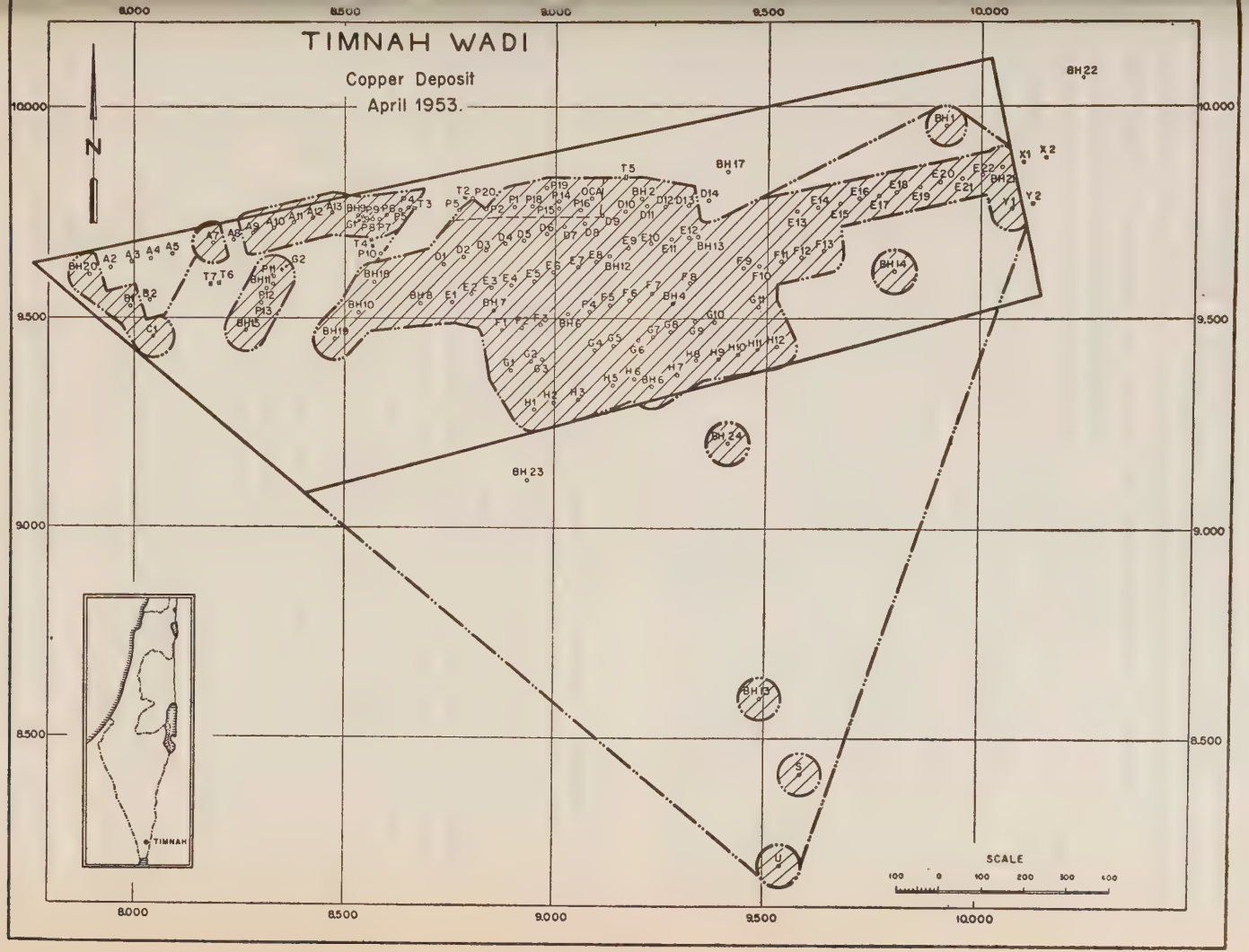
The deposit is classified into several varieties — Sandy, Shaly, and Zebra ores — which differ both physically and chemically. However, variation in structure and composition exists not only between varieties but also within the same variety. Copper content varies over the whole area and no *prima facie* evidence as to the possible existence of a regular shift along a certain direction or several directions is discernible. The major part of the exploration was concentrated in the northern part of the triangle and therefore our conclusions pertain to this trapezoidal area only (see map). Schematically in this study the area will be considered to be a rectangle. This rectangle possesses the following dimensions: The length of one side, coinciding with the base of the triangle, is 2000 metres, whereas the length of the other side, in the north-south direction, is 500 metres. A grid of bore-holes was drilled in this area, but in addition the outcrop site was explored by stripping and trenching; some shafts were also sunk. The southern part of the triangle, which is not analysed in this investigation, was explored by drilling a few bore-holes in order to trace the boundaries of the deposit.

The cylindrical cores obtained from the bore-holes by the drilling operation possess a diameter of a few inches. The portions of the core belonging to the layers above and below the mineralized layer were put aside, and the latter was then divided into two parts of equal volume, the plane of division containing the axis of the cylinder. One of these half-cylinders was stored away, while the other was divided into smaller parts each of 50 centimetres length; the planes of this division were perpendicular to the axis of the core. These smaller parts — the full length — were finely ground (separately) at the Israel Mining Industries Laboratories, Haifa, where the ore properties and characteristics were studied as well. It should be noted that the number of half-cylinders differed from core to core.

The ground ore as described above was systematically analysed for copper content by the standard iodometric analytical procedure.

Results of this survey were summarized and published by Baniel[1]. All data utilized in this study were taken from the survey.

Systematized information on details of copper distribution, the manifestation of possible trends and homogeneity or heterogeneity of copper content may be of some use to future mining activities. In particular, it is believed that because of the extreme variability of copper content over the whole explored region, data pertaining to average copper percentage may be of some value in the rational design of a mining plan.



Map of the drilling scheme

Israel Mining Industries, Haifa, April 1953

2. STATISTICAL METHODOLOGY

The modern viewpoint of the statistical method as developed by the school of R.A. Fisher has been summarized by Hald[2]:

"A statistical analysis can usually be divided into the following five steps:

"1. The planning of the investigation, in particular the sampling method and the number of observations.

"2. The specification, i.e. the formulation of a mathematical-statistical description, a model, of the observations.

"3. The estimation of the parameters pertaining to the model and derivation of the sampling distributions of these estimates.

"4. An examination of the agreement between the model and the observations.

"5. The real solution of the problem by the aid of the estimates of the parameters and tests of significance.

"These steps are not mutually independent . . ."

This study has very little to contribute to the first step formulated above. The decision to undertake a statistical analysis was made after the data pertaining to copper content were already known, i.e. prospecting and exploration preceded our analysis. Thus all data possess observational character and not experimental character, which, of course, would have been more desirable for a rational evaluation.

In order to draw valid conclusions, it is of the utmost importance to construct a model utilizing previous information and knowledge, professional or otherwise. Thus, were a generally accepted geological or geochemical theory on the formation of the deposit in existence, the task of a statistical analyst would be greatly facilitated. However, no such generally accepted theory exists at present, and the specification had to be restricted to a phenomenological description without any attempt at linking up this description with theoretical reasoning based on professional knowledge.

Fundamental to any development of a model—theoretical as well as phenomenological—is the notion of a population or universe. Such a population is typically made up of a very large number of elements or items—in fact an infinite number of elements, if this is conceptually possible. A number of elements drawn at random from the population forms a sample from which properties of the population are inferred with some degree of confidence. In the case under discussion a "copper-content population" is sought; however, there exists in this case no "natural" definition of a single population element. Under the given circumstances it is necessary to define—in a somewhat arbitrary manner—the single element as the copper percentage of one half-cylindrical core part as described in the Introduction. Thus, the nature of our population, i.e. its functional form and some of its parameters, is determined not only by the characteristics of the deposit, but also by the form of sampling, e.g. the diameter of the core, the length of the half-cylinder, etc. Again, while the existence of some arbitrariness has to be admitted, the adopted definition is the only reasonable procedure, considering the methods of exploration and chemical analysis.

From first principles it is clear that the most important parameter—the average copper percentage of the population—cannot depend on the definition of a single element or on the functional form of the population, so that the arbitrariness in the definition of a single element can introduce no bias. Another definition of the single element, were it forthcoming, might be capable of reducing the variability of sample means around the population mean and thus increase the precision of our estimates; however, their unbiasedness is not altered at all.

Most statistical techniques used in the analysis of data are based on the assumption that the elements of the sample under consideration have been drawn from the population in a random fashion, that is, the probability of obtaining any element from the population is independent of the probability of obtaining any other element. There are two objections to using the copper data on hand as if they were obtained in a random fashion. First, the selection of a bore-hole site depends to some extent on the nature of the terrain above the deposit; secondly, once a site had been selected and a hole drilled, more than one element was drawn from the bore-hole and the probability of obtaining the various elements thus became mutually dependent. The first objection cannot seriously affect our argument; the second point is much more serious. If some correlation exists between neighbouring elements, the sample cannot be considered as having been generated in a random fashion. Nevertheless, in the following we shall deal with the sample as if it were obtained by a true random process and in the final section we shall try to justify this assertion.

The basic problem of this investigation is to recognize whether the variations in copper content found over the whole region are:

(a) random fluctuations superimposed upon an underlying copper content which is essentially constant over the whole area,

(b) a manifestation of a regular shift in copper content in some directions,

(c) a manifestation of irregular shifts in copper content over the whole region.

Of these three alternatives, (a) or (c) are more easily affirmed, if true, than alternative (b). In fact, acceptance of the latter would call for some extraneous, professional (i.e. geological or geochemical) information and in the absence of such knowledge and theoretical insight we should have to have recourse to speculation or else to using the same data both for constructing and for testing the model—certainly an inadmissible procedure. Thus, only overwhelming evidence would induce us to accept alternative (b). We consider therefore (a) and (c) as the main competing alternative hypotheses in our statistical analysis.

If hypothesis (a) is found to be correct, we should be able to evaluate the average copper percentage of the whole explored deposit within quite close limits. If, on the other hand, hypothesis (c) is accepted, i.e. if the deposit is found to be *heterogeneous* with respect to average copper content, it would be desirable to subdivide the deposit into homogeneous sub-populations of maximum size. We would wish to partition the deposit in such a manner that the copper content is homogeneous, i.e. basically

constant, within each small region (except for random fluctuations), whereas heterogeneity with respect to average copper content prevails between these smaller regions. If such regions associated with homogeneous sub-populations can be found, confidence limits of sub-population means may be calculated and the properties of each smaller region be evaluated separately.

3. STATISTICAL ANALYSIS AND RESULTS

The proper statistical test procedure to decide between homogeneity and heterogeneity is the analysis of variance.

To carry out an analysis of variance it is necessary to proceed in five steps:

1. Partition of the deposit into several regions which are suspected to possess differing population means.
2. Selection of the variable which is considered to be normally distributed.
3. Separate testing of the samples drawn from all regions as to their compatibility with the assumption that the underlying distribution of the sub-population is normal.
4. Testing whether all sample variances are compatible with the assumption that they possess a common population variance.
5. The analysis of variance proper, i.e. testing whether all sample means are compatible with the assumption that they possess a common population mean (that there is really no difference between the regions).

The first two steps involve some *ad hoc* decisions to be discussed below:

The somewhat imperfect grid of bore-holes (see Map) is strongly associated with the east-west direction, that is, there are series of consecutive bore-holes running in this direction. Furthermore, the north-south direction is prominent in the deposit, since it is the one with the maximum dip. It was therefore decided to set up three schemes of partitioning into smaller regions, such that each scheme is associated with the N-S and E-W directions. Tables I, II, and III depict these schemes and the numbers inserted denote the size of the sample in each region, i.e. the number of analyses carried out for each region. This number exceeds the number of bore-holes in each region, since generally several analyses were made for each bore-hole, corresponding to different depths within the deposit.

TABLE I
First scheme of partitioning

Number of analyses
206
222
142
202
123
94
115

TABLE II
Second scheme of partitioning

Number of analyses			
276	276	276	276

TABLE III
Third scheme of partitioning

Number of analyses			
115	91	—	—
83	62	77	—
27	44	51	20
51	17	28	106
—	25	44	54
—	15	30	49
—	22	46	47

However, no account was taken of possible systematic variability as a function of depth within the deposit. Consideration of depth would have involved us in difficulties of conceptual and computational character. Also, appraising variability in the third dimension obviously would be of minor practical importance relative to the other two dimensions.

For convenience in the description of the deposit it was considered to possess pseudo-two-dimensional character, but in fact the deposit as a whole was being studied —the data originated from the analysis of the full length of the cores. It should be noted that in Table III not all spaces have been filled in, since no bore-holes were drilled in the corresponding regions. It was for this reason that no two-way classification analysis of variance was carried out on the third scheme.

The selection of the variable which is considered to be normally distributed—the second step enumerated above—necessitates some preliminary considerations. A naive approach would accept the copper percentage itself as the variable on which the operations of statistical test procedures should be performed. However, it is intuitively clear that small percentages possessing an appreciable variability cannot be normally distributed; rather we should expect a distribution which is skew to the right (Figure 1). This is so, since to the left of the average a natural barrier is found—

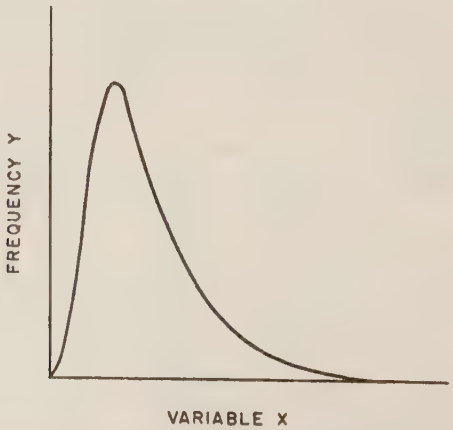


Figure 1. Skew distribution

there are no negative copper percentages. No such natural barrier is to be found to the right of the average. (In theory, a 100% copper content of the mineral represents such a barrier to the right, a natural upper limit of permissible values; it is, however, so far removed from the actual range of variability that its influence is negligible. The lower limit—0%—on the other hand, is very close to the actual range of variability, so that its influence cannot be discounted.) It was concluded, therefore, even before the computational stage of this analysis started, that copper percentage as such was not normally distributed and a preliminary graphical test of normality on probability paper—performed on all regional arrangements as envisaged in the three schemes—confirmed the existence of a skewness to the right in the frequency distribution of the data. The situation had to be remedied by transforming the data before subjecting them to statistical tests. Such transformations in comparable situations are not uncommon in many statistical applications and the logarithmic transformation was chosen as the operation that would "normalize" the data. This choice of a transformation function is relatively simple and introduces no additional parameters which would have to be estimated. It is very often selected when a distribution is skew to the right, as its application does away with non-permissible values to the left—the lower limit of the transformed variable being $-\infty$. Thus we may expect the transformation to symmetrize and normalize the data on hand. A preliminary graphical test of normality was carried out with the transformed data on probability paper and the data were found to be much closer to "normality" than before. The more rigorous test of normality envisaged in step 3 will be described later.

While in the first two steps—partition of the deposit and selection of the appropriate variable—somewhat arbitrary, though very reasonable, decisions had to be taken, the further procedure is made up of three objective tests. Normality, that is, compatibility of the hypothesis that the regional populations are distributed in a normal (or Gaussian) fashion with the actual findings in the various regions, is tested by K. Pearson's χ^2 - test of goodness of fit. If this hypothesis is not rejected (for each sub-population), we may proceed to the next test, examining the hypothesis that all sample variances—the observed variances in the various regions—are really derived from one common population variance; this common population variance may be considered to be a measure of the range of local random fluctuations in copper content. The appropriate procedure for this purpose is the application of Bartlett's test on the homogeneity of the variances. If there is no cogent reason to reject the hypothesis, the analysis of variance proper may be undertaken. This last test procedure is concerned with the two alternative hypotheses that the various sample means—the observed means in the different regions—are either derived from one common population mean or differ significantly among themselves; the appropriate procedure is the application of the variance ratio test or *F*-test. As these tests and their range of applicability are explained in all modern books on applied statistics, no original papers describing tests are quoted and only one comprehensive reference—Hald[2]—is cited again.

We may now summarize the situation by stating that the following three null hypotheses are being tested consecutively:

(a) All sub-populations are normal;

(b) All sub-populations have the same variance;

(c) All sub-populations have the same average.

A significant test result is tantamount to a statement that the null hypothesis is not tenable at the pre-assigned level of significance and must therefore be rejected. While theoretically such rejection of hypothesis (a) or (b) should preclude the continuation of the statistical analysis, it is well established that moderate deviations from normality as well as non-compliance with null hypothesis (b) do not affect the analysis of variance proper (the test of null hypothesis (c)) too seriously. It was decided, therefore, to try all three schemes of partitioning, and both copper percentage and its logarithm were chosen as feasible random variables; they were denoted as x (copper percentage) and z, which are related by

$$z = \log 10x = 1 + \log x \tag{1}$$

All in all, the complete procedure was carried out six times—one for each distinct combination of partitioning scheme and random variable. Table IV summarizes the test results of all combinations; the pre-assigned level of significance was 5% for the normality test and 1% for the other tests.

TABLE IV

Significance test results

	x – variable	z – variable
First scheme	a) All test results significant	a) 4 test results significant 3 test results not significant
	b) Test result significant	b) Test result significant
	c) Test result significant	c) Test result significant
Second scheme	a) All test results significant	a) 3 test results significant 1 test result not significant
	b) Test result significant	b) Test result not significant
	c) Test result significant	c) Test result significant
Third scheme	a) All test results significant	a) 1 test result significant 21 test results not significant
	b) Test result significant	b) Test result not significant
	c) Test result significant	c) Test result significant

Two features are manifest in this summary:

The means could not be considered as homogeneous—that is, as being derived from a common population mean—in any single combination.

One and only one combination gave non-significant test results on examining the two null hypotheses (a) and (b); this was the combination of the third scheme and

the z-variable. (There is one significant result—out of 22—of a normality test; this is what we should expect at the 5% significance level, if the null hypothesis (a) is correct. Also, addition of the χ^2 of all normality tests yields a non-significant result). This combination was then considered as being capable of yielding homogeneous regions. All further numerical analysis is based on this combination.

Tables V and VI comprise the sample means and sample variances respectively. Since the variances were found to be homogeneous, a pooled sample variance—an estimate of the common population variance—could be calculated. As this estimate is based on more than 1000 degrees of freedom—in this context a concept roughly equivalent to the total number of observations—no distinction was made between the population variance and its estimate.

TABLE V

Sample means (z – variable)

0.751	1.055	—	—
0.825	1.021	0.963	—
0.797	0.941	0.884	0.839
0.849	0.642	1.036	0.795
—	1.117	0.860	1.008
—	1.053	0.827	1.135
—	0.968	0.976	0.926

TABLE VI

Sample variances (z – variable)

0.225	0.139	—	—
0.167	0.198	0.128	—
0.083	0.149	0.123	0.107
0.106	0.151	0.129	0.127
—	0.145	0.092	0.121
—	0.097	0.162	0.159
—	0.115	0.113	0.082

Pooled sample variance: $\sigma^2 = 0.142$ (Degrees of freedom = 1082)

We now wish to transform the results given in Table V back to ordinary percentages and calculate confidence limits for each regional average copper percentage. The interpretation to be attached to such limits is that it may be stated with a high degree of confidence that the true regional population mean has been "bracketed" between two numbers; i.e. it is very unlikely (and just how unlikely should be established before the actual computation) that our method fails to set an interval of possible percentages among which the correct average copper percentage may be found.

It may be shown that a point estimate, a single best estimate, of the average regional copper content is given by

$$10^{\bar{z}+1.15\,\sigma^2} - 1 \qquad (2)$$

where $\bar{z}$ is the regional sample mean and σ^2 the pooled sample variance. The limits of the confidence interval are calculated on multiplication and division, respectively, of expression (2) by

$$10^{\sigma/\sqrt{n}\cdot u_{(1-\gamma)/2}} \tag{3}$$

where n is the size of the sample (number of observations in the region), γ the degree of confidence desired and $u_{(1-\gamma)/2}$ the value of the unit normal deviate pertaining to $(1-\gamma)/2$. It is defined by the following expression:

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{u_{(1-\gamma)/2}} e^{-u^2/2}\,du \tag{4}$$

Table VII summarizes the values of expression (2) for each region, that is the point estimate of the regional average. Table VIII comprises 95% confidence limits of average copper percentages for each region.

TABLE VII

Point estimates of copper percentage

0.822	1.655	—	—
0.973	1.528	1.337	—
0.914	1.272	1.115	1.006
1.028	0.638	1.581	0.909
—	1.905	1.055	1.484
—	1.647	0.979	1.989
—	1.352	1.378	1.229

TABLE VIII

95% confidence limits of copper percentage

0.96 0.70	1.98 1.39	—	—
1.17 0.81	1.90 1.23	1.62 1.10	—
1.27 0.66	1.64 0.98	1.42 0.88	1.47 0.69
1.31 0.81	0.96 0.42	2.18 1.15	1.07 0.77
	2.67	1.36	1.87
—	1.35	0.82	1.18
	2.56	1.34	2.54
—	1.06	0.72	1.56
	1.94	1.77	1.58
—	0.95	1.07	0.96

4. DISCUSSION AND CONCLUSION

In a sense Table VIII provides a solution of the problem on hand: evaluation of the deposit in terms of copper percentage. However, the question arises whether these results are not invalidated by the absence of true random sampling and the introduction of arbitrary assumptions—though based on reasonable considerations—at various stages of the analysis. The problem of arbitrary assumptions arises in statistical applications more often than is admitted. It must be pointed out, however, that in the case under discussion certain final results have justified some preliminary assumptions, e.g. the logarithmic transformations did normalize the various subpopulations (or regional populations) of the third scheme as well as homogenize the different sample variances. This is a fact of utmost importance on examining the validity of the analysis and its conclusion; in particular it should be remembered that the average sample size is approximately 50—certainly not a small number.

Non-significance of the normality tests and homogeneity of sample variances do not, in any event, give place to any suspicion that absence of true random sampling might have affected our results very seriously. Quantitative knowledge regarding correlation between neighbouring elements would have enabled us to calculate confidence intervals in a possibly more reliable fashion. If statistical work precedes the actual prospecting, an experimental design of exploration should be set up that enables calculating this correlation.

The concept of sub-population or regional population should not be accepted too literally in the sense that certain parameters are believed to exist which describe the populations and on the boundary lines these parameters abruptly change their value when we pass from one region to another. Rather, it should be thought that the parameters vary gradually even within the same region. It is desired to have regions of maximum size, such that the parametrical changes within the regions are small. The form and size of the regions is a matter of trial and error and in our analysis it became clear that the regions envisaged in the first scheme and in the second scheme were too large and had to be reduced. It may well be possible to construct homogeneous (or rather almost homogeneous) regions by a different system of sub-division possessing even more desirable properties, such as larger sizes of regions.

In the light of the above discussion we have to view the information contained in Table VIII. The degree of confidence—set at 95%—may have been reduced somewhat as a result of correlation between neighbouring elements and gradual parametrical changes within a supposedly homogeneous region. However, such reduction of degree of confidence can only be small, as large parametrical changes within a region would inflate the sample variances and the pooled sample variance, which is a measure of local random fluctuations. This increase of the variance enlarges also the confidence interval of the mean and thus counteracts the sources of confidence diminution.

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BOOK REVIEW

THE CONDENSED CHEMICAL DICTIONARY, by Arthur and Elizabeth Rose, 5th Edition, Reinhold Publishing Corporation, New York, 1956, pp. 1120.

This book contains some 30,000 entries on chemicals, trade-names, chemical terminology, etc. The data given generally include the properties of the substances, such as colour, solubility, specific gravity, b. p., m. p. and optical data, as well as a very short description of the method of preparation of the substance. Additional information is given on different available commercial grades, industrial uses, health hazards, shipping regulations and main suppliers.

This book should prove useful to people engaged in all phases of chemical industry, in production as well as in marketing.

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